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Specification and Drawings, as originally filed, with Application for Patent Serial No: **2,375,959**, on March 11, 2002, by **PAVEL CHEBEN AND MARIA LUISA CALVO**, for "Photosensitive Material and Method of Making Same".

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ABSTRACT OF THE DISCLOSURE

A photosensitive material, suitable for image-wise recording, e.g., holographic recording of data or other information, comprises an organic species in an organic/inorganic matrix, the organic species comprising a material having a refractive index which changes upon exposure to actinic radiation. The organic/inorganic matrix may be an organically modified host. The photosensitive material may be made using the sol-gel process.

PHOTOSENSITIVE MATERIAL AND METHOD OF MAKING SAME

BACKGROUND OF THE INVENTION

TECHNICAL FIELD

The invention relates to photosensitive materials and methods of making same and is especially, but not exclusively, applicable to photosensitive materials suitable for image-wise recording, for example holographic recording of data or other information.

BACKGROUND ART

There are many substances that are known to be photosensitive and suitable for holographic image recording. Those include silver halides, photopolymers, dichromated gelatins and photorefractive, ferromagnetic, photochromic and photodichroic materials. In these materials, temporary or permanent changes of real or imaginary part of refractive index are induced upon illumination of the material by actinic radiation and, typically, subsequent processing steps are required.

For high-resolution phase imaging such as that required in practical holographic data storage devices, there are several properties that an optimum recording material should exhibit. These include high dynamic range and sensitivity, high resolution, negligible shrinkage upon holographic exposure, low noise, phase image forming mechanism, image and dimensional stability, and fabricability into thick films and monoliths, to name the most relevant ones. However, to meet all these properties in a single material is a significant challenge that has not been satisfactorily overcome up to present and lack of such medium is currently considered in the art as one of the main hurdles in development of practical holographic data storage systems.

Existing techniques

Photopolymers are believed to be promising holographic recording materials for applications such as display or security holograms, Write-Once Read-Many times (WORM) holographic memories, or Holographic Optical Elements (HOEs). A number of photopolymerizable systems have been developed up to present, such as those disclosed in US patents 3,658,526; 4,942,112; 4,959,284 and 4,994,347 assigned to E. I Du Pont

de Nemours and Company, US patents 4,588,664; 4,696,876 and 4,970,129 assigned to Polaroid Corporation, US patent 3,993,485 assigned to Bell Telephone Laboratories, US patent 4,173,474 assigned to Cannon Kabushiki Kaisha, and US patent 3,694,218 assigned to Hughes Aircraft Company. Another promising class of materials are porous glasses impregnated by photopolymerizable materials such as those disclosed in Spanish patent P9700217 assigned to the Instituto Nacional de Tecnica Aeroespacial, Japanese patents JP6148880a assigned to Nippon Sheet Glass Co. Ltd. and JP61141476A assigned to Sony Corp.

Limitations or drawbacks of existing techniques

Application of photopolymers to volume holography and data storage is severely limited due to their limited thickness, high shrinkage during holographic exposure and need for solvent processing. A recording medium of millimeter thickness or more and exhibiting high photoinduced refractive index change is required to achieve high storage density by recording multiple volume holograms, separated from each other by the Bragg effect, in the same spatial location.

The most important limitations are imposed by organic polymeric binders that limit thickness of the medium, usually to less than a few hundred microns, and temperature- and light-induced dimensional changes that can distort the holograms and degrade the fidelity with which the stored images can be retrieved. An approach to prepare thicker photopolymers is to use resins consisting of two independent photopolymerisable systems such as those disclosed in M. L. Schilling et al., Chem. Mater. 11, 247 (1999) or W. L. Wilson et al., Opt. Quant. Electr. 32, 393 (2000), in which matrix-forming oligomers are first precured to a gel state and then the hologram is recorded by photoinduced polymerization of monomers dissolved in the resin. However, this approach does not simultaneously achieve high dimensional stability and maximum photoinduced refractive index change. To increase the rigidity of the material, higher levels of precuring are required, which decreases diffusional mobility of the monomer in the resin and degrades holographic properties of the photopolymer. In addition, some monomeric species are inevitably consumed (polymerized) during the precuring step, which in turn reduces

dynamic range of the holographic recording and, ultimately, limits the data storage capacity of the material.

Porous glasses such as those fabricated by sol-gel technique appear to be promising for data storage as they can typically be fabricated as bulk monoliths. However, the materials disclosed up to present, including Spanish patent P9700217 assigned to the Instituto Nacional de Tecnica Aeroespacial, Japanese patents JP6148880A assigned to Nippon Sheet Glass Co. Ltd. and JP61141476A assigned to Sony Corp. suffer from drawbacks ranging from insufficient sensitivity and dynamic range for practical applications to insufficient optical quality and thickness.

SUMMARY OF THE INVENTION:

The present invention seeks to at least ameliorate the disadvantages of such known materials, or at least provide an alternative.

According to the present invention, a photosensitive material comprises at least one organic species in an organic/inorganic matrix, the at least one organic species comprising a material having a refractive index which changes upon exposure to actinic radiation.

The organic species may comprise an efficient organic photosensitive and photoinitiating species together with a monomer or a mixture of monomers.

The organic/inorganic matrix may comprise an organically modified "glassy" host with the organic spores dispersed therein and/or chemically-bonded thereto. The organically modified host of embodiments of the present invention may provide desired optical quality and physical and chemical stability.

The organic species may be bonded to the organic/inorganic matrix by covalent bonding.

Alternatively, the organic species may be a dispersion in the organic/inorganic material.

The at least one organic species can be impregnated or entrapped as a guest within inorganic host matrixes here.

According to a second aspect of the invention, there is provided a method of making a photosensitive material comprising the steps of forming an organic/inorganic

matrix containing at least one organic species having a refractive index that changes on exposure to actinic radiation.

Preferably, in embodiments of either aspect of the invention, the photosensitive material is formed using a sol-gel process.

The preferred manufacturing process, namely the sol-gel technique, is well known in the art, and has been widely used in the preparation of oxide glasses by hydrolysis and condensation of metal alkoxides since the first synthesis of silica from silicon alkoxide was reported by Ebelmen in 1844. Given that the sol-gel process can take place at room temperature, it may be used to incorporate an organic species, e.g., organic molecules with low thermal stability, into an organic/inorganic matrix, e.g., an inorganic "glassy" host.

The organic species may be dispersed in an organically-modified host over domains of several nanometers, which results in a material exhibiting very low optical scattering, even if the refractive indices of the organic species differ from that of the host matrix.

The host matrix is a crucial component affecting physical properties of the photosensitive material, such as its rigidity, environmental stability, elimination of dimensional changes upon holographic exposure, and maximum achievable thickness. It also affects optical properties of the composite, including bulk refractive index, optical homogeneity and photoinduced refractive index change.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description, in conjunction with the accompanying drawings, of preferred embodiments of the invention, which are described by way of example only.

BRIEF DESCRIPTION OF DRAWINGS:

Figure 1 illustrates geometry used for glass characterization by a plane grating recording; and

Figure 2 illustrates grating growth measurement in photosensitive glass.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Embodiments of the invention disclosed herein include a photosensitive material and a method of fabricating same that provide a high resolution and stable phase image recording properties. Using the sol-gel process, the material may be prepared by incorporating photosensitive and photopolymerizable organic species, as dopants, into a liquid glass precursor sol and the latter transformed via controlled hydrolysis and polycondensation reactions into a solid material of a high optical quality. High optical quality and excellent imaging properties such as high dynamic range, sensitivity, resolution and image stability may be achieved by a combination of efficient photosensitive and phototopolymerizable species with an organically modified host matrix.

The organic/inorganic matrix may comprise a hybrid network synthesized by using low molecular weight organo alkoxysilanes as one or more of the precursors for the sol-gel reaction in which organic groups are introduced within an inorganic network through the ≡Si-C- bond. Alternatively, the organic/inorganic matrix can be formed via the co-condensation of functionalized oligomers or polymers with metal alkoxides in which chemical bonding is established between inorganic and organic phases.

The organic/inorganic matrix can also be synthesized through the formation of inorganic species within a polymer matrix. Specifically, inorganic species, generally in the form of particles with a characteristic size of a few hundred angstroms, can be generated in situ within the polymer matrix by first swelling cross-linked, ionomeric, or crystalline polymeric host with a compatible solution containing metal alkoxides followed by the promotion of the sol-gel reaction of the inorganic.

Yet another alternative would be to obtain the organic/inorganic matrix by either the infiltration of previously formed oxide gels with polymerizable organic monomers or the mixing of polymers with metal alkoxides in a common solvent.

The matrix can also be formed by interpenetrating networks and simultaneous formation of inorganic and organic phases. By using triethoxysliane $R'Si(OR)_3$ or diethoxysilanes $R'R''Si(OR)_2$ as the precursor with R' and R" being a polymerizable group such as an epoxy group, an organic network can be formed within the inorganic network by either photochemical or thermal curing of such groups.

Yet another method is to form the matrix from inorganic/organic simultaneous interpenetrating networks, where both inorganic glass and polymer formation occur concurrently. Such transparent composites are synthesized through a synchronous application of the aqueous ring-opening metathesis polymerization of cyclic alkenyl monomers and the hydrolysis and condensation of metal alkoxides.

Other ways of making the matrix include employing polymerizable monomers as the cosolvents such that all the components (i.e. the monomers and sol-gel precursors) contribute either to the inorganic matrix or to the organic polymer matrix, which together form the organic/inorganic matrix, to avoid large scale shrinkage.

Yet another approach is to use intercalation and self-assembling properties of layered ceramics, particularly those based on the 2:1 layered silicates consisting of two-dimensional layers formed by sandwiching two SiO2 tetrahedral sheets to an edge shared octahedral sheet.

In a preferred embodiment of this invention, the organic/inorganic matrix is achieved by copolymerization of epoxysilanes such as (3-glycidoxypropyl)trialkoxysilane with a tetraalkoxysilane in the presence of dispersed photosensitive, photoinitiating and photopolymerizable species.

A wide variety of free radical or cationic initiators can be used to initiate polymerization while the photoactivation of initiator molecules can be achieved by a number of sensitizing molecules well known in the art. A review of photopolymerization processes can be found for example in Dye Sensitized Photopolymerization by D. F. Eaton, Adv. in Photochemistry, Vol. 13, D. H. Volman et al. Eds., Wiley-Interscience, New York, pp. 427-487 (1986). A large number of sensitizers and initiators providing blue, green, red and near infra-red sensitivity can be used in the implementations of this invention, including halogen-substituted acetophenones, chromophore-substituted triazines, azo dies, benzoin ethers, ketals, o-acylated oximino ketones, acyl phosphine oxides, aromatic ketones, hexaarylbisimidazoles, bis(p-dialkylaminobenzilidene)ketones, thioxanthones, ketocoumarins, 9-phenylacridine, die-sensitized systems such as xantene, acridinium, phenazine and thiazine dyes in combination with activators such as amines,

sulfinates, enolates, carboxylates and organotine compounds, dye-borate complexes, ferrocenium salts, aluminate complexes, and protic acid generators.

Preferred sensitizers and initiators for use in embodiments of this invention include organometallic systems such as dicyclopentadienyltitanocenes, in particular bis(pentafluorophenyl)titanocene, titanocene/N-phenylglycine, and bis(μ^5-2,4-cyclopentadien-1-yl)-bis-[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]titanium; and bis(p-dialkylaminobenzilidene)ketones in combination with a HABI (hexaarylbisimidazole) initiating systems such as 2,2',4,4',5,5'-hexaarylbisimidazole with charge transfer agents such as 2-mercaptobenzoxazole. Concentration of the sensitizer and initiator in the matrix is from 0.001 to 10%, preferably from 0.01 to 3% depending on thickness of the material.

A wide variety of monomers or oligomers can be used in embodiments of this invention. Acrylate and methacrylate monomers are preferred because of their high propagation and low termination rates. Furthermore, monomers with high molar refraction are preferred as they maximize the refractive index change per one diffusing monomer molecule upon holographic exposure.

Advantageously, the monomers have good solubility in silica sol without degrading the optical and mechanical properties of the composite. A large number of suitable monomers are available including ethylene glycol phenyl ether acrylate, 2-phenoxyethyl acrylate, N-vinylcarbazol, p-chlorophenyl acrylate, hexanediol diacrylate, vinyl benzoate, N-vinylcarbazole, tert-butyl hydroperoxide, hexanediol diacrylate, 2,4,6-tribromophenyl acrylate, N-vinylcarbazole, phenyl acrylate, 2-phenylethyl acrylate, and pentachlorophenyl acrylate. Other suitable monomers are those capable of cationic ring opening polymerization (CROP). Such CROP monomers have two or more cyclohexene oxide groups linked through siloxane chain segments, for example such as 1,3-bis[2-(3{7-oxabicyclo[4.1.0]heptyl})ethyl]-tetramethyl disiloxane. Polymerization of such monomers can be initiated by strong protic acids that are generated during the photo decomposition of, for example, sulfonim or iodonium salts. Concentration of the monomers in the glass is from 10 to 80%, preferably 20-50%.

Examples and experimental results

The following examples and experimental results are used to illustrate, but not limit, the scope of this invention.

In this example, the photosensitivity in blue and green parts of the visible spectrum is achieved by a free radical generating titanocene photoinitiator, specifically bis(μ^5-2,4-cyclopentadien-1-yl)-bis-[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl] titanium. A low concentration of the photoinitiator in the glass, 0.4-0.8 wt% depending on the glass thickness, is chosen to assure a uniform light absorption through the entire volume of the glass. This also helps eliminate spurious gratings produced by diffusion of photoinitiator molecules, resulting from its own concentration gradients induced by holographic exposure. An ethylenic unsaturated monomer ethylene glycol phenyl ether acrylate is used at a concentration in the glass of 40 wt%. Both photoinitiator and monomer were added into sol-gel solution of (3-glycidoxypropyl)trimethoxysilane with tetramethoxysilane and hydrofluoric acid as catalyst prior to the gelation point. After stirring the solution for 20 minutes at 40 °C, a homogeneous solution was obtained. It was then cast into Teflon (TM) vials and allowed to gel and dry for 10 days at 60°C. Dry monoliths were polished to optical-grade slabs of thickness ~1mm. Films of ~260 μm thickness were prepared by casting 0.1 ml of the solution onto a borosilicate glass plate. The films were dried for 5 days at 60°C.

Figure 1 shows the geometry used for glass characterization by a plane grating recording; collimated writing beams 1 and 2 of wavelength λ_1 (514.5 nm) were arranged to incide on the glass symmetrically with respect to the sample normal. The angle between the writing beams was $2\alpha = 3°$ and $34°$ for gratings of a period $\Lambda = 9.8\ \mu$m and $0.9\ \mu$m, respectively. The glass refractive index was measured as $n = 1.47$ by a prism-coupling technique. The grating was probed by diffraction of the read-out beam 3 of wavelength λ^2 (632.8 nm) into the beam 4 (first Bragg order). The angle of incidence of the beam 3 was $\beta = 1.8°$ and $20.6°$ for $\Lambda = 9.8\ \mu$m and $0.9\ \mu$m, respectively. At this angle, the first-order Bragg condition $\mathbb{k}_3 + \mathbb{K} = \mathbb{k}_4$ was satisfied; $\mathbb{K}$ being the grating vector and $\mathbb{k}_3$ and $\mathbb{k}_4$ being the wave vectors of the beams 3 and 4, respectively.

To characterize holographic performance of the glass, plane gratings were recorded in the glass by two mutually coherent plane-wave writing beams 1 and 2 (Fig. 1). The writing beams (wavelength 514.5 nm, beam diameter 1.5 cm, intensity of each beam 50 mW/cm^2) were from an Ar-ion laser operating in a single longitudinal and transversal mode. The grating growth was studied during and after the holographic exposure by diffraction of read-out beam 3.

The angle of incidence β of the read-out beam was set to satisfy the first-order Bragg condition at which the intensity of the first-order diffracted beam (beam 4) and thus, diffraction efficiency η, is maximized. To minimize a possible photochemical influence of the read-out beam, a low-intensity (0.8 mW/cm^2) beam of 632.8 nm wavelength (from a He-Ne laser) at which the absorption of the photoinitiator is low, was used. In the experiment, polarization of the writing and read-out beams was perpendicular ('s' polarization) to the plane defined by the sample normal and wave vectors of the writing beams.

After the holographic exposure, the sample was kept in the dark for 15 minutes to allow any dark reactions to subside. The photoreaction was then completed by uniformly exposing the sample 5 minutes to UV light (wavelength 254 nm, intensity 1350 (W/cm^2) from a low-pressure mercury vapor lamp. The diffraction efficiency dependence on the angle of incidence was measured by detuning β from the Bragg condition. This measurement yields the grating angular selectivity θ defined as full-width at half-maximum (FWHM) of the angular selectivity curve. The refractive index modulation amplitude Δn and effective thickness of the grating were calculated from the diffraction efficiency and angular selectivity data using Kogelnik's coupled-wave theory (H. Kogelnik, *Bell Syst. Tech. J.* 48, p. 2909, 1969).

Figure 2 shows dependence of the diffraction efficiency η and refractive index modulation Δn (Fig. 2 inset) on exposure when a holographic grating of a period $\Lambda = 9.8$ μm is recorded in a glass monolith of 950 μm thickness with photoinitiator content of 0.4 wt%. A short induction period of virtually no growth of η can be observed at the beginning of the exposure. This is due to rapid destruction of the thermal inhibitors and consumption of dissolved molecular oxygen by the photogenerated free radicals. Once the

inhibiting species have been consumed, polymerization of the monomer starts. η increases with the exposure and reaches a maximum of 98% at $E = 0.23$ J/cm^2 yielding a refractive index modulation $\Delta n = 3 \cdot 10^{-4}$.

Further increase of the exposure leads to an oscillatory evolution of η, typical for volume gratings. Steady-state diffraction efficiency and $\Delta n = 1.3 \cdot 10^{-3}$ are achieved at the exposure $E \sim 1.5$ J/cm^2, which corresponds to a sensitivity $S = \Delta n / E = 8.6 \cdot 10^{-4}$ cm^2/J. A dynamic sensitivity $S^* = d(\Delta n)/dE = 1.8 \cdot 10^{-3}$ cm^2/J was achieved in the region of exposure 0.1- 0.35 J/cm^2. These values of Δn, S and S* are the highest reported to date in a photopolymerizable material of similar thickness (R. A. Lessard and G. Manivannan, Proc. SPIE 2405, p. 2, 1995; J. Marotz, Appl. Phys. B 37, p. 181, 1985; G. J. Steckman et al., Opt. Lett. 23, p. 1310, 1998; P. Cheben et al., Opt. Lett. 21, p. 1857, 1996; Spanish patent P9700217 assigned to the Instituto Nacional de Tecnica Aeroespacial.)

In the angular selectivity experiment $\Delta\theta = 10$ mrad was measured, yielding an effective grating thickness of 941 μm. This shows that the grating was recorded practically in entire depth of the monolith. Gratings were also recorded in films of 260 μm thickness with photoinitiator content of 0.8 wt%. There was achieved $\Delta n = 4.5 \cdot 10^{-3}$ for $E = 0.72$ J/cm^2 and thus, a sensitivity $S = 6.2 \cdot 10^{-3}$ cm^2/J, for gratings of a period $\Lambda = 0.9$ μm. Again, these values by far exceed both the refractive index modulation and sensitivity disclosed to date in photopolymerizable systems developed for applications in holographic data storage.

Figure 2 illustrates grating growth measurement in photosensitive glass in which: Writing beams: wavelength 514.5 nm, intensity of each beam 50 mW/cm^2; read-out beam: wavelength 632.8 nm, intensity 0.8 mW/cm^2. All beams are 's'-polarized. Main Figure, exposure dependence of the diffraction efficiency η (circles). η was calculated as the intensity ratio of the light diffracted into the first Bragg order (beam 4) to the intensity of the read-out beam 3, the latter being measured at its exit from the sample prior to the holographic exposure. The solid lines are guides to the eye. Inset, exposure dependence of the refractive index grating amplitude Δn (squares) obtained from the coupled-wave theory for volume transmission gratings.

The mechanism of grating formation can be explained by the models developed for holographic photopolymers (W. S. Colburn, Appl. Opt. 10, p. 1636, 1971; G. Zhao and P. Mouroulis, J. Mod. Opt. 41, p. 1929, 1994). The monomer polymerization starts and proceeds preferentially in the light regions of the illumination pattern. The depletion of the monomer in the light regions sets-up a spatial concentration gradient resulting in a diffusional flux of monomer molecules from the dark to the light regions, along the grating vector. In addition, it is well known in the art that acrylic monomers shrink on polymerization. As the monomer molecules, separated at van der Walls distances, are converted to covalently bonded polymer, voids are created in the light regions, and the resulting capillary forces draw the fresh monomer from the dark to the light regions. This process continues until either there is no more unreacted monomer in the dark regions or transport of monomer is hindered by increased rigidity of the polymer in the polymerized regions. Ultimately, permanent compositional and density changes and associated refractive index modulation are induced in the material. It is known that the diffusion of monomer is a critical mechanism in the formation of holographic gratings in photopolymerizable materials. A porous matrix advantageously provides for efficient liquid monomer transport.

Embodiments of the present invention provide a new class of photosensitive material providing a significant advance in the field of research on holographic recording materials. The material has unprecedented sensitivity and refractive index modulation capability for a thick photopolymerizable material. The holograms stored in the material are permanent and stable; the constancy of Δn over a period of 12 months at room temperature having been demonstrated. An additional advantage of the material, as compared to holographic photopolymers, is that it can be easily fabricated into samples of high optical quality and thickness of several millimeters. The failure of the prior art attempts to make photopolymers of such a thickness with required holographic properties has been considered the main obstacle in development of holographic write-once memories. In contrast, photosensitive materials embodying the present invention exhibit both excellent holographic properties and ease of fabrication into thick films or monoliths of high optical quality, as required for holographic storage applications.

Advantageously, characteristics required for volume holographic recording, including photosensitivity, high refractive index modulation, desired material thickness, high optical quality, and dimensional stability, are achieved by embodiments of the invention which employ a combination of an organic species, for example an organic photoinitiating and monomeric species, within an organic/inorganic matrix, for example a hybrid organic-inorganic or organically-modified material (glass). A further advantage is that photosensitive materials embodying the present invention can be polished to optical-grade.

Although the above-described preferred embodiments of the invention refer to phase holographic recording, the invention is applicable to amplitude holographic recording and, indeed, other forms fo image-wise refractive index and/or absorption.

The preferred manufacturing process, namely the sol-gel technique, is well known in the art, and has been widely used in the preparation of oxide glasses by hydrolysis and condensation of metal alkoxides since the first synthesis of silica from silicon alkoxide was reported by Ebelmen in 1844. Given that the sol-gel process can take place at room temperature, it may be used to incorporate an organic species, e.g., organic molecules with low thermal stability, into an organic/inorganic matrix, e.g., an inorganic "glassy" host.

The host/matrix is a crucial component affecting physical properties of the photosensitive material, such as its rigidity, environmental stability, elimination of dimensional changes upon holographic exposure, and maximum achievable thickness. It also affects optical properties of the composite, including bulk refractive index, optical homogeneity and photoinduced refractive index change.

Although embodiments of the invention have been described and illustrated in detail, it is to be clearly understood that the same is by way of illustration and example only and not to be taken by way of the limitation, the spirit and scope of the present invention being limited only by the appended claims.

CLAIMS

What is claimed is:

1. A photosensitive material comprising at least one organic species in an organic/inorganic matrix, the organic at least one species comprising a material having a refractive index which changes upon exposure to actinic radiation.

2. A photosensitive material according to claim 1, wherein the organic species comprises an efficient organic photosensitive and photoinitiating species together with a monomer or a mixture of monomers.

3. A photosensitive material according to claim 1 or 2, wherein organic/inorganic matrix comprises an organically modified glassy host with the organic species dispersed therein and/or chemically-bonded thereto.

4. A photosensitive material according to claim 3, wherein the organic species is bonded to the organic/inorganic matrix by covalent bonding.

5. A photosensitive material according to claim 4, wherein the organic species comprises a dispersion in the organic/inorganic material.

6. A photosensitive material according to claim 1, wherein the at least one organic species is entrapped as a guest within the inorganic host matrixes.

7. A photosensitive material according to any of claims 1 to 6, wherein the organically modified host comprises a second organic species.

8. A photosensitive material according to any one of claims 1 to 7, wherein the photosensitive material comprises a product of a sol-gel process.

9. A photosensitive material according to any of claims 1 to 8, wherein the first organic species is selected from the group comprising halogen-substituted acetophenones, chromophore-substituted triazines, azo dies, benzoin ethers, ketals, o-acylated oximino ketones, acyl phosphine oxides, aromatic ketones, hexaarylbisimidazoles, bis(p-dialkylaminobenzilidene)ketones, thioxanthones, ketocoumarins, 9-phenylacridine, die-sensitized systems such as xantene, acridinium, phenazine and thiazine dyes in combination with activators such as amines, sulfinates, enolates, carboxylates and organotine compounds, dye-borate complexes, ferrocenium salts, aluminate complexes, protic acid generators such as sulfonium or iodonium salts capable of initiating cationic polymerization, and organometallic systems such as dicyclopentadienyltitanocenes, in particular bis(pentafluorophenyl)titanocene, titanocene/N-phenylglycine, and bis(μ^5-2,4-cyclopentadien-1-yl)-bis- [2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]titanium; and bis(p-dialkylaminobenzilidene) ketones in combination with a HABI (hexaarylbisimidazole) initiating system such as 2,2',4,4',5,5'-hexaarylbisimidazole with charge transfer agents such as 2-mercaptobenzoxazole.

10. A photosensitive material according to any of claims 1 to 8, wherein the first organic species is selected from the monomers capable of free radical or cationic polymerization, respectively.

11. A photosensitive material according to claim 10, wherein the monomers have good solubility in silica sol without degrading the optical and mechanical properties of the composite.

12. A photosensitive material according to claim 11, wherein the monomers are selected from the group comprising ethylene glycol phenyl ether acrylate, 2-phenoxyethyl acrylate, N-vinylcarbazol, p-chlorophenyl acrylate, hexanediol diacrylate, vinyl benzoate, N-vinylcarbazole, tert-butyl hydroperoxide, hexanediol diacrylate, 2,4,6-tribromophenyl acrylate, N-vinylcarbazole, phenyl acrylate, 2-phenylethyl acrylate, pentachlorophenyl acrylate, and monomers capable of cationic ring opening polymerization (CROP) with two

or more cyclohexene oxide groups linked through siloxane chain segments.

13. A material according to claim 1, wherein the organic/inorganic matrix comprises a material synthesized using low molecular weight organo alkoxysilanes as one or more of the precursors for a sol-gel reaction in which organic groups are introduced within an inorganic network through the ≡Si-C- bond.

14. A material according to claim 1, wherein the organic/inorganic matrix is formed by means of a co-condensation of functionalized oligomers or polymers with metal alkoxides in which chemical bonding is established between inorganic and organic phases.

15. A material according to claim 1, wherein the organic/inorganic matrix material is synthesized through the formation of inorganic species within a polymer matrix.

16. A material according to claim 1, wherein inorganic species, generally in the form of particles with a characteristic size of a few hundred angstroms, are generated in situ within the polymers by first swelling cross-linked, ionomeric, or crystalline polymeric host with a compatible solution containing metal alkoxides followed by the promotion of the sol-gel reaction of the inorganics.

17. A material according to claim 1, wherein the organic/inorganic matrix material is obtained by either the infiltration of previously formed oxide gels with polymerizable organic monomers or the mixing of polymers with metal alkoxides in a common solvent.

18. A material according to claim 1, wherein the organic/inorganic matrix material is formed by impregnation of porous oxide gels with organics followed by an *in situ* polymerization initiated by thermal or irradiation methods.

19. A material according to claim 1, wherein the material is formed by hydrolysis and condensation of metal alkoxide carried out in the presence of polymers and

organic/inorganic matrix material is formed by trapping polymers within the oxide gel network.

20. A material according to claim 1, wherein the organic/inorganic matrix material is formed by impregnating or entrapping organic material as a guest within the inorganic host matrix.

21. A material according to claim 1, wherein the organic/inorganic matrix material is formed by interpenetrating networks and simultaneous formation of inorganic and organic phases.

22. A material according to claim 1, wherein the organic/inorganic matrix material is formed as an organic network within an inorganic network by either photochemical or thermal curing of such groups. using triethoxysliane $R'Si(OR)_3$ or diethoxysilanes $R'R''Si(OR)_2$ as the precursor with R' and R" being a polymerizable group such as an epoxy group,

23. A material according to claim 1, wherein the organic/inorganic matrix material is formed as inorganic/organic simultaneous interpenetrating networks, where both inorganic glass and polymer formation occur concurrently.

24. A material according to claim 22, synthesized through a synchronous application of the aqueous ring-opening metathesis polymerization of cyclic alkenyl monomers and the hydrolysis and condensation of metal alkoxides.

25. A material according to claim 1, employing polymerizable monomers as the cosolvents such that all the components contribute either to the silica network or to the organic polymer.

26. A material according to claim 1, using intercalation and self assembling properties

of layered ceramics.

27. A material according to claim 26, wherein the layered ceramics are based on 2:1 layered silicates comprising two-dimensional layers formed by sandwiching two SiO2 tetrahedral sheets to an edge shared octahedral sheet.

28. A material according to claim 3, wherein organic modification of the matrix material is achieved by copolymerization of epoxysilanes such as (3-glycidoxypropyl)trialkoxysilane with a tetraalkoxysilane in the presence of dispersed photosensitive, photoinitiating and photopolymerizable species.

29. A method of making a photosensitive material comprising the steps of forming an organic/inorganic matrix containing at least one organic species having a refractive index that changes on exposure to actinic radiation.

30. A method according to claim 29, wherein the method comprises a sol-gel process.

31. A method according to claim 29, wherein the organic/inorganic matrix is synthesized using using low molecular weight organo alkoxysilanes as one or more of the precursors for a sol-gel reaction in which organic groups are introduced within an inorganic network through the ≡Si-C- bond.

32. A method according to claim 29, wherein the organic/inorganic matrix is formed by means of a co-condensation of functionalized oligomers or polymers with metal alkoxides in which chemical bonding is established between inorganic and organic phases.

33. A method according to claim 29, wherein the organic/inorganic matrix material is synthesized through the formation of inorganic species within a polymer matrix.

34. A method according to claim 29, wherein inorganic species, generally in the form

of particles with a characteristic size of a few hundred angstroms, are generated in situ within the polymers by first swelling cross-linked, ionomeric, or crystalline polymeric host with a compatible solution containing metal alkoxides followed by the promotion of the sol-gel reaction of the inorganics.

35. A method according to claim 29, wherein the organic/inorganic matrix material is obtained by either the infiltration of previously formed oxide gels with polymerizable organic monomers or the mixing of polymers with metal alkoxides in a common solvent.

36. A method according to claim 35, wherein the organic/inorganic matrix material is formed by impregnation of porous oxide gels with organics followed by an *in situ* polymerization initiated by thermal or irradiation methods.

37. A method according to claim 35, wherein the hydrolysis and condensation of metal alkoxide are carried out in the presence of polymers and organic/inorganic matrix material is formed by trapping polymers within the oxide gel network.

38. A method according to claim 29, further comprising the step of impregnating or entrapping organic material as a guest within the inorganic host matrix.

39. A method according to claim 29, wherein the organic/inorganic matrix material is formed by interpenetrating networks and simultaneous formation of inorganic and organic phases.

40. A method according to claim 29, wherein the organic/inorganic matrix material is formed as an organic network within the inorganic network by either photochemical or thermal curing of such groups. using triethoxysliane $R'Si(OR)_3$ or diethoxysilanes $R'R''Si(OR)_2$ as the precursor with R' and R" being a polymerizable group such as an epoxy group,

41. A method according to claim 29, wherein the organic/inorganic matrix material is formed as inorganic/organic simultaneous interpenetrating networks, where both inorganic glass and polymer formation occur concurrently.

42. A method according to claim 41, wherein said material is synthesized through a synchronous application of the aqueous ring-opening metathesis polymerization of cyclic alkenyl monomers and the hydrolysis and condensation of metal alkoxides.

43. A method according to claim 31, employing polymerizable monomers as the cosolvents such that all the components contribute either to the inorganic network or to the organic polymer.

44. A method according to claim 29, using intercalation and self assembling properties of layered ceramics.

45. A method according to claim 44, wherein the layered ceramics are based on 2:1 layered silicates consisting of two-dimensional layers formed by sandwiching two SiO2 tetrahedral sheets to an edge shared octahedral sheet.

46. A method according to claim 29, wherein organic modification of the matrix material is achieved by copolymerization of epoxysilanes such as (3-glycidoxypropyl)trialkoxysilane with a tetraalkoxysilane in the presence of dispersed photosensitive, photoinitiating and photopolymerizable species.

47. A method according to claim 46, wherein the photoinitiating species comprises a salt capable of initiating cationic polymerization.

48. A method according to claim 47, wherein the salt comprises sulfonium or iodonium.

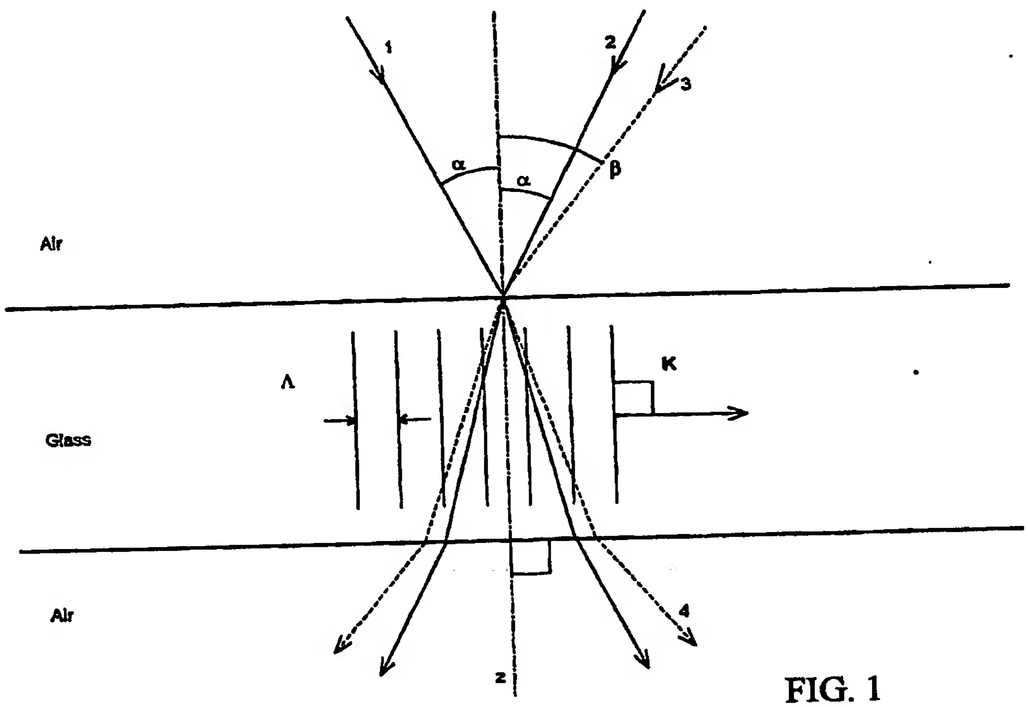

FIG. 1

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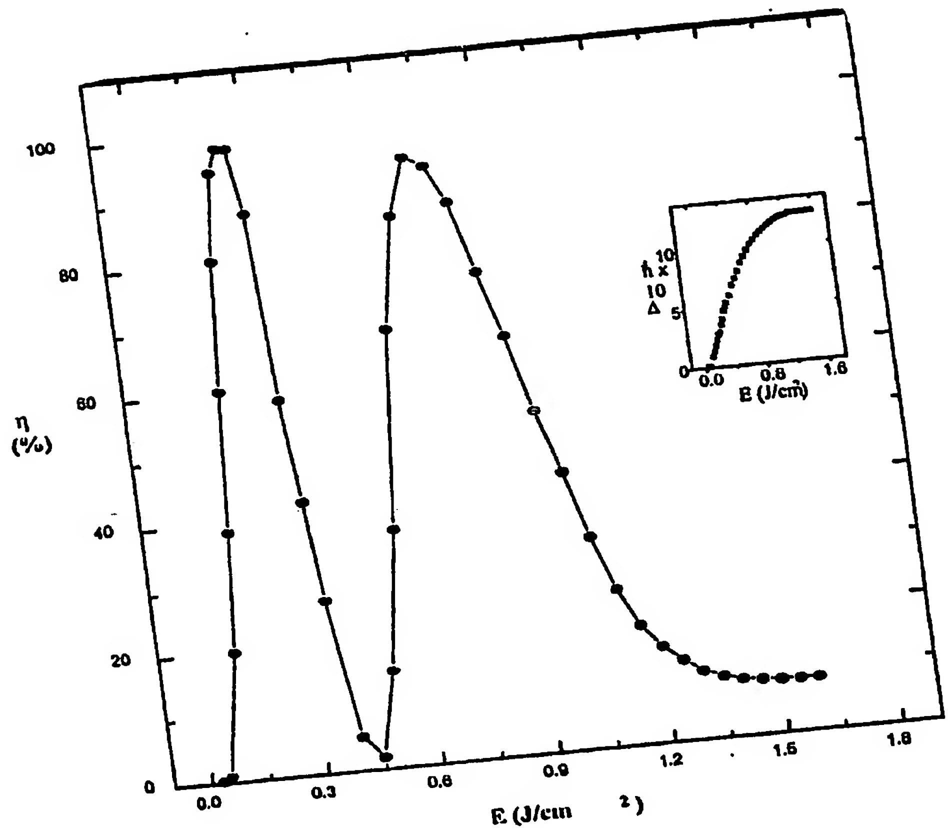

FIG. 2

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